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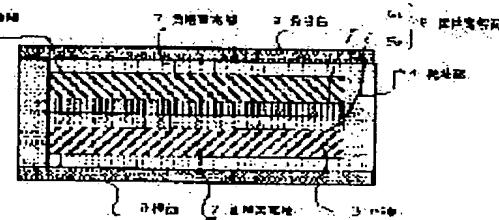
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(54) SOLID ELECTROLYTIC CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To solve a problem that adhering of an electrode and a solid electrolyte is difficult and an interface resistance of the electrode and the solid electrolyte is high in the prior art.

SOLUTION: A solid electrolytic cell is sealed in an exterior package by intervening a solid electrolyte between a positive electrode formed of a spinel-system lithium manganate and a negative electrode formed of a spinel-system lithium titanate, wherein the solid electrolyte is formed of a sintered body formed of Li_2MnO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ ($M=Al$ or Ga , $0 \leq x \leq 0.4$, $0 < y \leq 0.6$) and a sintered body formed of Li_2TiO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ ($M=Al$ or Ga , $0 \leq x \leq 0.4$, $0 < y \leq 0.6$), and at the same time, the sintered body formed of Li_2MnO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ ($M=Al$ or Ga , $0 \leq x \leq 0.4$, $0 < y \leq 0.6$) is arranged in the positive electrode side and the sintered body formed of Li_2TiO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ ($M=Al$ or Ga , $0 \leq x \leq 0.4$, $0 < y \leq 0.6$) is arranged on the negative electrode side.



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CLAIMS

[Claim(s)]

[Claim 1] In the solid electrolyte cell which pinched the solid electrolyte with the positive electrode which consists of a spinel system manganic acid lithium, and the negative electrode which consists of spinel system lithium titanate, and was enclosed in the sheathing package. The sintered compact which consists said solid electrolyte of Li_2MnO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (M =aluminum or Ga, $0 \leq x \leq 0.4$, $0 < y \leq 0.6$), While forming with the sintered compact which consists of Li_2TiO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (M =aluminum or Ga, $0 \leq x \leq 0.4$, $0 < y \leq 0.6$) said positive-electrode side -- said Li_2MnO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (or it Ga(s) M =aluminum --) the sintered compact which consists of $0 \leq x \leq 0.4$ and $0 < y \leq 0.6$ -- arranging -- said negative-electrode side -- said Li_2TiO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (or it Ga(s) M =aluminum --) The solid electrolyte cell characterized by arranging $0 \leq x \leq 0.4$ and the sintered compact which consists of $0 < y \leq 0.6$.

[Claim 2] The solid electrolyte cell characterized by forming said negative electrode with $Li_{1+x}Ti_{2-x}O_4$ ($0.25 \leq x \leq 0.40$) sintered compact while forming said positive electrode with $Li_{1+x}Mn_{2-x}O_4$ ($0.05 \leq x \leq 0.2$) or $Li_{1+x}Ni_yMn_{2-x-y}O_4$ ($0 \leq x \leq 0.2$, $0.4 \leq y \leq 0.6$) sintered compact.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the solid electrolyte cell which pinched the solid electrolyte with the positive electrode and the negative electrode, and was enclosed in the sheathing package about a solid electrolyte cell.

[0002]

[Description of the Prior Art] There is a remarkable thing in high-performance-izing and a miniaturization of a notebook computer in recent years, a cellular phone, etc. of a portable electronic device. The cell used for these pocket device requires the much more formation of a high energy consistency and the much more miniaturization.

[0003] As what meets such a demand, the lithium secondary battery using the ejection and insertion of a lithium ion is studied briskly.

[0004] However, since the conventional lithium secondary battery is using nonaqueous electrolyte, it has the problem which cannot be disregarded on the product safety of a liquid spill or ignition of the electrolytic solution.

[0005] In order to solve such a problem, development of the solid electrolyte cell not using the electrolytic solution is considered entirely.

[0006] Lithium ion conductivity crystallized glass with the presentation expressed with $Li_{1+x}M_xTi_{2-x}Si_yP_3-yO_{12}$ ($M=$ aluminum or Ga, $0 < x < 0.4$, $0 < y < 0.6$) indicated by JP,10-97811,A, for example as a solid electrolyte is advocated. This crystallized glass has the advantage that there are few grain boundaries, therefore grain boundary resistance is low, and as a result high lithium ion conductivity called 1×10^{-3} S/cm is obtained, in order to carry out a crystal deposit by heat treatment, after fusing a configuration raw material.

[0007] However, in JP,10-97811,A, the processing very in an elevated temperature is needed from heat treatment for melting being performed at 1450 degrees C, and heat treatment for a crystal deposit being performed in two steps, 800 degrees C and 1000 degrees C. On the other hand, the electrode active material used with a lithium secondary battery has many which are heat-treated at the temperature of 700 to at most 900 degrees C. Therefore, since the heat treatment temperature at the time of joining an electrode and a solid electrolyte must be doubled with an electrode active material, the solid electrolyte cell which junction to an electrode and the solid electrolyte which consists of crystallized glass was difficult, and has joined both good for the moment is not obtained.

[0008] Moreover, in JP,5-299101,A, although the solid electrolyte which sintered $Li_{1+(4-n)}xM_xTi_{2-x}(PO_4)_3$ ($2 n=$ when a univalent or divalent cation and M of M are univalent cations and $n=1$ and M are divalent cations $x 0.1-0.5$) is also advocated, since this sintering temperature is also as high as 1000 to 1200 degrees C, the junction to an electrode is difficult.

[0009] On the other hand, an electrode and a solid electrolyte are stuck and the approach for offering the low solid electrolyte cell of interfacial resistance is proposed.

[0010] For example, in JP,6-111831,A, it has advocated making a lithium compound react to the front face of the positive electrode which consists of MnO_2 or an alkali-metal manganese multiple oxide, and making it generate Li_2MnO_3 of a solid electrolyte. According to this approach,

the adhesion of a positive electrode and a solid electrolyte is good, and since the touch area is large, there is an advantage that interfacial resistance is low.

[0011] However, in JP,6-111831,A, since the capacity which an active material originally has since the ionic conductivity of a solid electrolyte is low cannot fully be pulled out upwards and the metal lithium is used for a negative electrode, it depends for the contact to a negative electrode and a solid electrolyte on the plasticity of a metal lithium, and interfacial resistance has the problem that it cannot but become high, compared with a positive-electrode side.

[0012] This invention is made in view of the trouble of such a conventional technique, and junction to an electrode and a solid electrolyte aims at offering the solid electrolyte cell which canceled the conventional trouble that the interfacial resistance of an electrode and a solid electrolyte was large difficultly.

[0013]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, in the solid electrolyte cell concerning this invention In the solid electrolyte cell which pinched the solid electrolyte with the positive electrode which consists of a spinel system manganic acid lithium, and the negative electrode which consists of spinel system lithium titanate, and was enclosed in the sheathing package The sintered compact which consists said solid electrolyte of Li_2MnO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (M=aluminum or Ga, $0 \leq x \leq 0.4$, $0 \leq y \leq 0.6$), While forming with the sintered compact which consists of Li_2TiO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (M=aluminum or Ga, $0 \leq x \leq 0.4$, $0 \leq y \leq 0.6$) said positive-electrode side -- said Li_2MnO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (or it Ga(s) M=aluminum --) It is characterized by having arranged $0 \leq x \leq 0.4$ and the sintered compact which consists of $0 \leq y \leq 0.6$, and arranging in said negative-electrode side said sintered compact which consists of Li_2TiO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (M=aluminum or Ga, $0 \leq x \leq 0.4$, $0 \leq y \leq 0.6$).

[0014] While forming said positive electrode in the above-mentioned solid electrolyte cell with $Li_{1+x}Mn_{2-x}O_4$ ($0.05 \leq x \leq 0.2$) or $Li_{1+x}Ni_yMn_{2-x-y}O_4$ ($0 \leq x \leq 0.2$, $0.4 \leq y \leq 0.6$) sintered compact, it is desirable to form said negative electrode with $Li_{1+x}Ti_{2-x}O_4$ ($0.25 \leq x \leq 0.40$) sintered compact.

[0015]

[Embodiment of the Invention] Hereafter, the operation gestalt of this invention is explained. the sectional view in which drawing 1 shows the example of a configuration of the solid electrolyte cell of this invention -- it is -- 1 -- a positive-electrode can and 2 -- for the insulating section and 5, as for a negative electrode and 7, a solid electrolyte and 6 are [a positive-electrode current collection layer and 3 / a positive electrode and 4 / a negative-electrode current collection layer and 8] negative-electrode cans. A sheathing package consists of a positive-electrode can 1, a negative-electrode can 8, and the insulating section 4.

[0016] A positive electrode 3 consists of the sintered compact of a spinel system manganic acid lithium. There is $Li_{1+x}Mn_{2-x}O_4$ ($0.05 \leq x \leq 0.2$) or $Li_{1+x}Ni_yMn_{2-x-y}O_4$ ($0 \leq x \leq 0.2$, $0.4 \leq y \leq 0.6$) in such a spinel system manganic acid lithium.

[0017] Here, if the effectiveness of suppressing the expansion contraction at the time of charge and discharge is not enough if x of $Li_{1+x}Mn_{2-x}O_4$ ($0.05 \leq x \leq 0.2$) is smaller than 0.05, and x is larger than 0.2, since the fall of charge-and-discharge capacity is remarkable, the advantage used for a positive electrode 3 will be spoiled.

[0018] Moreover, although it is the positive-electrode ingredient of high potential, since nickel will not have dissolved and $Li_{1+x}Ni_yMn_{2-x-y}O_4$ ($0 \leq x \leq 0.2$, $0.4 \leq y \leq 0.6$) will generate an impurity phase if sufficient high potential will not be obtained as compared with $Li_{1+x}Mn_{2-x}O_4$ ($0.05 \leq x \leq 0.2$) if this y is smaller than 0.4, and y becomes 0.6 or more, it is not desirable.

[0019] A negative electrode 6 consists of the sintered compact of spinel system lithium titanate. There is $Li_{1+x}Ti_{2-x}O_4$ ($0.25 \leq x \leq 0.40$) in such spinel system lithium titanate.

[0020] The effectiveness of suppressing the expansion contraction at the time of charge and discharge here if x of $Li_{1+x}Ti_{2-x}O_4$ ($0.25 \leq x \leq 0.40$) is smaller than 0.25 is not enough, and since a lithium will not have dissolved and an impurity phase will be generated if x is larger than 0.4, it is not desirable.

[0021] The approach of sintering, after making the water or the organic solvent in which (1)

shaping assistant was dissolved in order to produce a positive electrode 3 and a negative electrode 6 distribute active material fine particles, adjusting a slurry, adding a direct or shaping assistant, corning the approach of judging and sintering after carrying out tape forming of this slurry and drying, or (2) active-material fine particles, supplying to metal mold and carrying out pressing with a press machine etc. is used.

[0022] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.

[0023] A solid electrolyte 5 consists of sintered compact 5a which consists of Li_2MnO_3 and $\text{Li}_{1+x+y}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{aluminum or Ga, } 0 \leq x \leq 0.4, 0 < y \leq 0.6$), and sintered compact 5b which consists of Li_2TiO_3 and $\text{Li}_{1+x+y}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{aluminum or Ga, } 0 \leq x \leq 0.4, 0 < y \leq 0.6$). Li_2MnO_3 and $\text{Li}_{1+x+y}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (or it Ga(s) $\text{M}=\text{aluminum --} 0 \leq x \leq 0.4$ and sintered compact 5a which consists of $0 < y \leq 0.6$ are arranged in a positive-electrode 3 side, and sintered compact 5b which consists of Li_2TiO_3 and $\text{Li}_{1+x+y}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{aluminum or Ga, } 0 \leq x \leq 0.4, 0 < y \leq 0.6$) is arranged in a negative-electrode 6 side.

[0024] $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0.05 \leq x \leq 0.2$) or $\text{Li}_{1+x}\text{Ni}_{y}\text{Mn}_{2-x-y}\text{O}_4$ ($0 \leq x \leq 0.2, 0.4 \leq y \leq 0.6$) which is the active material ingredient with which Li_2MnO_3 constitutes a positive electrode 3 here, It is used in order to join $\text{Li}_{1+x+y}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{aluminum or Ga, } 0 \leq x \leq 0.4, 0 < y \leq 0.6$) which is the ingredient which constitutes solid electrolyte 5a.

[0025] Moreover, Li_2TiO_3 is used in order to join $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($0.25 \leq x \leq 0.40$) which is the active material ingredient which constitutes a negative electrode 6, and $\text{Li}_{1+x+y}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{aluminum or Ga, } 0 \leq x \leq 0.4, 0 < y \leq 0.6$) which is the ingredient which constitutes solid electrolyte 5b.

[0026] The approach of sintering, after making the water or the organic solvent in which (1) shaping assistant was dissolved in order to produce a solid electrolyte 5 (5a, 5b) distribute solid electrolyte fine particles, adjusting a slurry, adding a direct or shaping assistant, corning the approach of judging and sintering after carrying out tape forming of this slurry and drying, or (2) solid-electrolyte fine particles, supplying to metal mold and carrying out pressing with a press machine etc. is used.

[0027] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.

[0028] The sintering conditions of a solid electrolyte 5, a positive electrode 3, and a negative electrode 6 are suitably chosen from 30 minutes within the limits of 30 hours according to the synthetic conditions of the presentation of an active material and a solid electrolyte, an active material, and a solid electrolyte, or the size of a sintered compact at 500 to 900 degrees C.

[0029] The positive-electrode current collection layer 2 and the negative-electrode current collection layer 7 are arranged for contact to the positive-electrode can 1, a positive electrode 3, or the negative-electrode can 8 and a negative electrode 6, and current collection, for example, consist conductive ingredients, such as gold, silver, copper, aluminum, nickel, and carbon, of vacuum evaporation or the thin film which carried out sputtering.

[0030] It is arranged in order that the positive-electrode can 1 and the negative-electrode can 8 may prevent inhibition of the charge-and-discharge reaction by the moisture in atmospheric air, and in order to use as each terminal of a positive electrode 3 and a negative electrode 6, for example, the sheet metal of metals, such as aluminum, copper, nickel, stainless steel, and titanium, is used.

[0031] In order that the insulating section 4 may prevent the short circuit of a positive electrode 3 and a negative electrode 6, it is arranged, for example, macromolecules, such as polyethylene, polypropylene, and polyimide, are used.

[0032] A sheathing package consists of a positive-electrode can 1, the insulating section 4, and a negative-electrode can 8.

[0033]

[Example 1] The laminating of the positive-electrode Plastic solid which consists of $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$, and the solid electrolyte Plastic solid by the side of the positive electrode which consists

of Li₂MnO₃/Li_{1.31}aluminum_{0.3}Ti_{1.7}Si_{0.1}P_{2.99}O₁₂=10/90wt% is carried out. The laminating of the negative-electrode Plastic solid which consists of Li_{1.33}Ti 1.67O₄, and the solid electrolyte Plastic solid by the side of the negative electrode which consists of Li₂TiO₃/Li_{1.31}aluminum_{0.3}Ti_{1.7}Si_{0.1}P_{2.99}O₁₂=10/90wt% is carried out. Furthermore The solid electrolyte layer which consists of Li₂MnO₃/Li_{1.31}aluminum_{0.3}Ti_{1.7}Si_{0.1}P_{2.99}O₁₂=10/90wt%, and the solid electrolyte layer by the side of the negative electrode which consists of Li₂TiO₃/Li_{1.31}aluminum_{0.3}Ti_{1.7}Si_{0.1}P_{2.99}O₁₂=10/90wt% The solid electrolyte cell component was produced by carrying out a laminating so that it may ****, and processing at 850 degrees C for 10 hours.

[0034] As for the size of the produced solid electrolyte cell component, for the positive electrode, 250 micrometers and a solid electrolyte were [a total of 10 micrometers and the negative electrode of phi20mm and thickness] 250 micrometers.

[0035] After vapor-depositing gold to both sides of a solid electrolyte cell component and forming a phi18mm current collection layer in them, the solid electrolyte cell was produced by inserting in into a polyethylene ring with the outer diameter of 25mm, a bore [of 20.5mm], and a height of 550 micrometers, and inserting and carrying out thermocompression bonding to the aluminum sheet metal of two sheets in an argon.

[0036]

[The example 1 of a comparison] The solid electrolyte cell component was produced by carrying out the laminating of the positive-electrode Plastic solid which consists of Li_{1.1}Mn 1.9O₄, the solid electrolyte Plastic solid which consists of Li_{1.31}aluminum_{0.3}Ti_{1.7}Si_{0.1}P_{2.99}O₁₂, and the negative-electrode Plastic solid which consists of Li_{1.33}Ti 1.67O₄, and processing it at 850 degrees C for 10 hours.

[0037] The made solid electrolyte cell component had the weak solid electrolyte layer, therefore was that in which a positive electrode and a negative electrode tend to peel.

[0038] As for the size of the produced solid electrolyte cell component, for the positive electrode, 250 micrometers and a solid electrolyte were [a total of 10 micrometers and the negative electrode of phi20mm and thickness] 250 micrometers.

[0039] After vapor-depositing gold to both sides of a solid electrolyte cell component and forming a phi18mm current collection layer in them, dealing with it carefully, the solid electrolyte cell was produced by inserting in into a polyethylene ring with the outer diameter of 25mm, a bore [of 20.5mm], and a height of 550 micrometers, and inserting and carrying out thermocompression bonding to the aluminum sheet metal of two sheets in an argon.

[0040] Charge-and-discharge capacity was measured with the current density of 100microA/cm² about the produced solid electrolyte cell. The result is shown in Table 1.

[0041]

[Table 1]

実測容量 (正極基準)	実測容量/理論容量比 (正極基準)
実施例 1 : 10.5 mAh/g	95.5%
比較例 1 : 動作しない	—

[0042] The positive-electrode sintered compact which consists of Li_{1.1}Mn 1.9O₄ as Table 1 shows, The solid electrolyte sintered compact which consists of Li_{1.31}aluminum_{0.3}Ti_{1.7}Si_{0.1}P_{2.99}O₁₂, As opposed to the example 1 of a comparison which consists of negative-electrode sintered compacts which consist of Li_{1.33}Ti 1.67O₄ not showing charge-and-discharge actuation While arranging the solid electrolyte which changes from Li₂MnO₃/Li_{1.31}aluminum_{0.3}Ti_{1.7}Si_{0.1}P_{2.99}O₁₂=10/90wt% to the positive-electrode side which consists of Li_{1.1}Mn 1.9O₄ The solid electrolyte cell of the example 1 which arranged the solid electrolyte which changes from Li₂TiO₃/Li_{1.31}aluminum_{0.3}Ti_{1.7}Si_{0.1}P_{2.99}O₁₂=10/90wt% to the negative-electrode side which consists of Li_{1.33}Ti 1.67O₄ shows charge-and-discharge actuation.

[0043] This is added to sintering of a solid electrolyte having the inadequate example 1 of a comparison. Junction to the positive electrode which consists of Li_{1.1}Mn 1.9O₄ in an example 1

to a thing with the high interfacial resistance of an electrode and a solid electrolyte, and Li_2MnO_3 in a solid electrolyte, Junction to the negative electrode which consists of $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$, and Li_2TiO_3 in a solid electrolyte, Junction to Li_2MnO_3 in a positive-electrode side solid electrolyte, and $\text{Li}_{1.31}\text{aluminum}_{0.3}\text{Ti}_{1.7}\text{Si}_{0.1}\text{P}_{2.99}\text{O}_{12}$, And each of junction to Li_2TiO_3 in a negative-electrode side solid electrolyte and $\text{Li}_{1.31}\text{aluminum}_{0.3}\text{Ti}_{1.7}\text{Si}_{0.1}\text{P}_{2.99}\text{O}_{12}$ is good. The solid electrolyte sintered compact with high ionic conductivity with a sufficient therefore degree of sintering was not only obtained, but Li_2MnO_3 in a positive-electrode side solid electrolyte dissolves to $\text{Li}_{1.31}\text{aluminum}_{0.3}\text{Ti}_{1.7}\text{Si}_{0.1}\text{P}_{2.99}\text{O}_{12}$ in $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ in a positive electrode, and a solid electrolyte. When Li_2TiO_3 in a negative-electrode side solid electrolyte dissolves to $\text{Li}_{1.31}\text{aluminum}_{0.3}\text{Ti}_{1.7}\text{Si}_{0.1}\text{P}_{2.99}\text{O}_{12}$ in $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$ in a negative electrode, and a solid electrolyte, it is because the interfacial resistance of an electrode and a solid electrolyte is reduced.

[0044] In addition, the same effectiveness is checked even if it uses $\text{Li}_{1}\text{nickel}_{0.5}\text{Mn}_{1.5}\text{O}_4$ for positive active material.

[0045]

[Effect of the Invention] As mentioned above, the sintered compact which consists a solid electrolyte of Li_2MnO_3 and $\text{Li}_{1+x+y}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{aluminum or Ga, } 0 \leq x \leq 0.4, 0 < y \leq 0.6$) according to the solid electrolyte cell concerning this invention, While forming with the sintered compact which consists of Li_2TiO_3 and $\text{Li}_{1+x+y}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{aluminum or Ga, } 0 \leq x \leq 0.4, 0 < y \leq 0.6$) a positive-electrode side -- above-mentioned Li_2MnO_3 and $\text{Li}_{1+x+y}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (or it Ga(s) $\text{M}=\text{aluminum}$ --) the sintered compact which consists of $0 \leq x \leq 0.4$ and $0 < y \leq 0.6$ -- arranging -- a negative-electrode side -- above-mentioned Li_2TiO_3 and $\text{Li}_{1+x+y}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (or it Ga(s) $\text{M}=\text{aluminum}$ --) From having arranged $0 \leq x \leq 0.4$ and the sintered compact which consists of $0 < y \leq 0.6$ Junction to the positive electrode which consists of $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$, and Li_2MnO_3 in a solid electrolyte, Junction to the negative electrode which consists of $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$, and Li_2TiO_3 in a solid electrolyte, Junction to Li_2MnO_3 in a positive-electrode side solid electrolyte, and $\text{Li}_{1.31}\text{aluminum}_{0.3}\text{Ti}_{1.7}\text{Si}_{0.1}\text{P}_{2.99}\text{O}_{12}$, According to each of junction to Li_2TiO_3 in a negative-electrode side solid electrolyte and $\text{Li}_{1.31}\text{aluminum}_{0.3}\text{Ti}_{1.7}\text{Si}_{0.1}\text{P}_{2.99}\text{O}_{12}$ being good, the cell which operates normally also under current density high enough can be offered.

[0046] Moreover, since the negative electrode was formed with spinel system lithium titanate and it is small to extent which there is no expansion contraction at the time of the charge and discharge of these active materials, or hardly becomes a problem while forming a positive electrode with a spinel system manganic acid lithium, the nature cell of solid-state electrification in which the charge-and-discharge behavior which contact of the interface of an electrode and a solid electrolyte is not spoiled, therefore was stabilized is shown can be offered.

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TECHNICAL FIELD

[Field of the Invention] Especially this invention relates to the solid electrolyte cell which pinched the solid electrolyte with the positive electrode and the negative electrode, and was enclosed in the sheathing package about a solid electrolyte cell.

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EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, the sintered compact which consists a solid electrolyte of Li_2MnO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (M =aluminum or Ga, $0 \leq x \leq 0.4$, $0 \leq y \leq 0.6$) according to the solid electrolyte cell concerning this invention. While forming with the sintered compact which consists of Li_2TiO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (M =aluminum or Ga, $0 \leq x \leq 0.4$, $0 \leq y \leq 0.6$) a positive-electrode side -- above-mentioned Li_2MnO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (or it Ga(s) M =aluminum --) the sintered compact which consists of $0 \leq x \leq 0.4$ and $0 \leq y \leq 0.6$ -- arranging -- a negative-electrode side -- above-mentioned Li_2TiO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (or it Ga(s) M =aluminum --) From having arranged $0 \leq x \leq 0.4$ and the sintered compact which consists of $0 \leq y \leq 0.6$ Junction to the positive electrode which consists of $Li_{1.1}Mn_{1.9}O_4$, and Li_2MnO_3 in a solid electrolyte, Junction to the negative electrode which consists of $Li_{1.33}Ti_{1.67}O_4$, and Li_2TiO_3 in a solid electrolyte, Junction to Li_2MnO_3 in a positive-electrode side solid electrolyte, and $Li_{1.31}aluminum_{0.3}Ti_{1.7}Si_{0.1}P_{2.99}O_{12}$, According to each of junction to Li_2TiO_3 in a negative-electrode side solid electrolyte and $Li_{1.31}aluminum_{0.3}Ti_{1.7}Si_{0.1}P_{2.99}O_{12}$ being good, the cell which operates normally also under current density high enough can be offered.

[0046] Moreover, since the negative electrode was formed with spinel system lithium titanate and it is small to extent which there is no expansion contraction at the time of the charge and discharge of these active materials, or hardly becomes a problem while forming a positive electrode with a spinel system manganic acid lithium, the nature cell of solid-state electrification in which the charge-and-discharge behavior which contact of the interface of an electrode and a solid electrolyte is not spoiled, therefore was stabilized is shown can be offered.

[Translation done.]

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TECHNICAL PROBLEM

[Description of the Prior Art] There is a remarkable thing in high-performance-izing and a miniaturization of a notebook computer in recent years, a cellular phone, etc. of a portable electronic device. The cell used for these pocket device requires the much more formation of a high energy consistency and the much more miniaturization.

[0003] As what meets such a demand, the lithium secondary battery using the ejection and insertion of a lithium ion is studied briskly.

[0004] However, since the conventional lithium secondary battery is using nonaqueous electrolyte, it has the problem which cannot be disregarded on the product safety of a liquid spill or ignition of the electrolytic solution.

[0005] In order to solve such a problem, development of the solid electrolyte cell not using the electrolytic solution is considered entirely.

[0006] Lithium ion conductivity crystallized glass with the presentation expressed with $Li_{1+x}M_xTi_{2-x}Si_yP_3-yO_{12}$ ($M=$ aluminum or Ga, $0 \leq x \leq 0.4$, $0 < y \leq 0.6$) indicated by JP,10-97811,A, for example as a solid electrolyte is advocated. This crystallized glass has the advantage that there are few grain boundaries, therefore grain boundary resistance is low, and as a result high lithium ion conductivity called 1×10^{-3} S/cm is obtained, in order to carry out a crystal deposit by heat treatment, after fusing a configuration raw material.

[0007] However, in JP,10-97811,A, the processing very in an elevated temperature is needed from heat treatment for melting being performed at 1450 degrees C, and heat treatment for a crystal deposit being performed in two steps, 800 degrees C and 1000 degrees C. On the other hand, the electrode active material used with a lithium secondary battery has many which are heat-treated at the temperature of 700 to at most 900 degrees C. Therefore, since the heat treatment temperature at the time of joining an electrode and a solid electrolyte must be doubled with an electrode active material, the solid electrolyte cell which junction to an electrode and the solid electrolyte which consists of crystallized glass was difficult, and has joined both good for the moment is not obtained.

[0008] Moreover, in JP,5-299101,A, although the solid electrolyte which sintered $Li_{1+(4-n)}xM_xTi_{2-x}(PO_4)_3$ ($2 n=$ when a univalent or divalent cation and M of M are univalent cations and $n=1$ and M are divalent cations $x 0.1-0.5$) is also advocated, since this sintering temperature is also as high as 1000 to 1200 degrees C, the junction to an electrode is difficult.

[0009] On the other hand, an electrode and a solid electrolyte are stuck and the approach for offering the low solid electrolyte cell of interfacial resistance is proposed.

[0010] For example, in JP,6-111831,A, it has advocated making a lithium compound react to the front face of the positive electrode which consists of MnO_2 or an alkali-metal manganese multiple oxide, and making it generate Li_2MnO_3 of a solid electrolyte. According to this approach, the adhesion of a positive electrode and a solid electrolyte is good, and since the touch area is large, there is an advantage that interfacial resistance is low.

[0011] However, in JP,6-111831,A, since the capacity which an active material originally has since the ionic conductivity of a solid electrolyte is low cannot fully be pulled out upwards and the metal lithium is used for a negative electrode, it depends for the contact to a negative electrode and a solid electrolyte on the plasticity of a metal lithium, and interfacial resistance

has the problem that it cannot but become high, compared with a positive-electrode side. [0012] This invention is made in view of the trouble of such a conventional technique, and junction to an electrode and a solid electrolyte aims at offering the solid electrolyte cell which canceled the conventional trouble that the interfacial resistance of an electrode and a solid electrolyte was large difficultly.

[Translation done.]

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MEANS

[Means for Solving the Problem] In order to attain the above-mentioned purpose, in the solid electrolyte cell concerning this invention In the solid electrolyte cell which pinched the solid electrolyte with the positive electrode which consists of a spinel system manganic acid lithium, and the negative electrode which consists of spinel system lithium titanate, and was enclosed in the sheathing package The sintered compact which consists said solid electrolyte of Li_2MnO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (M=aluminum or Ga, $0 \leq x \leq 0.4$, $0 \leq y \leq 0.6$), While forming with the sintered compact which consists of Li_2TiO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (M=aluminum or Ga, $0 \leq x \leq 0.4$, $0 \leq y \leq 0.6$) said positive-electrode side -- said Li_2MnO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (or it Ga(s) M=aluminum --) It is characterized by having arranged $0 \leq x \leq 0.4$ and the sintered compact which consists of $0 \leq y \leq 0.6$, and arranging in said negative-electrode side said sintered compact which consists of Li_2TiO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ (M=aluminum or Ga, $0 \leq x \leq 0.4$, $0 \leq y \leq 0.6$).

[0014] While forming said positive electrode in the above-mentioned solid electrolyte cell with $Li_{1+x}Mn_{2-x}O_4$ ($0.05 \leq x \leq 0.2$) or $Li_{1+x}Ni_yMn_{2-x-y}O_4$ ($0 \leq x \leq 0.2$, $0.4 \leq y \leq 0.6$) sintered compact, it is desirable to form said negative electrode with $Li_{1+x}Ti_{2-x}O_4$ ($0.25 \leq x \leq 0.40$) sintered compact.

[0015]

[Embodiment of the Invention] Hereafter, the operation gestalt of this invention is explained. the sectional view in which drawing 1 shows the example of a configuration of the solid electrolyte cell of this invention -- it is -- 1 -- a positive-electrode can and 2 -- for the insulating section and 5, as for a negative electrode and 7, a solid electrolyte and 6 are [a positive-electrode current collection layer and 3 / a positive electrode and 4 / a negative-electrode current collection layer and 8] negative-electrode cans. A sheathing package consists of a positive-electrode can 1, a negative-electrode can 8, and the insulating section 4.

[0016] A positive electrode 3 consists of the sintered compact of a spinel system manganic acid lithium. There is $Li_{1+x}Mn_{2-x}O_4$ ($0.05 \leq x \leq 0.2$) or $Li_{1+x}Ni_yMn_{2-x-y}O_4$ ($0 \leq x \leq 0.2$, $0.4 \leq y \leq 0.6$) in such a spinel system manganic acid lithium.

[0017] Here, if the effectiveness of suppressing the expansion contraction at the time of charge and discharge is not enough if x of $Li_{1+x}Mn_{2-x}O_4$ ($0.05 \leq x \leq 0.2$) is smaller than 0.05, and x is larger than 0.2, since the fall of charge-and-discharge capacity is remarkable, the advantage used for a positive electrode 3 will be spoiled.

[0018] Moreover, although it is the positive-electrode ingredient of high potential, since nickel will not have dissolved and $Li_{1+x}Ni_yMn_{2-x-y}O_4$ ($0 \leq x \leq 0.2$, $0.4 \leq y \leq 0.6$) will generate an impurity phase if sufficient high potential will not be obtained as compared with $Li_{1+x}Mn_{2-x}O_4$ ($0.05 \leq x \leq 0.2$) if this y is smaller than 0.4, and y becomes 0.6 or more, it is not desirable.

[0019] A negative electrode 6 consists of the sintered compact of spinel system lithium titanate. There is $Li_{1+x}Ti_{2-x}O_4$ ($0.25 \leq x \leq 0.40$) in such spinel system lithium titanate.

[0020] The effectiveness of suppressing the expansion contraction at the time of charge and discharge here if x of $Li_{1+x}Ti_{2-x}O_4$ ($0.25 \leq x \leq 0.40$) is smaller than 0.25 is not enough, and since a lithium will not have dissolved and an impurity phase will be generated if x is larger than 0.4, it is not desirable.

[0021] The approach of sintering, after making the water or the organic solvent in which (1) shaping assistant was dissolved in order to produce a positive electrode 3 and a negative electrode 6 distribute active material fine particles, adjusting a slurry, adding a direct or shaping assistant, corning the approach of judging and sintering after carrying out tape forming of this slurry and drying, or (2) active-material fine particles, supplying to metal mold and carrying out pressing with a press machine etc. is used.

[0022] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.

[0023] A solid electrolyte 5 consists of sintered compact 5a which consists of Li_2MnO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_3-yO_{12}$ ($M=$ aluminum or Ga, $0 \leq x \leq 0.4$, $0 < y \leq 0.6$), and sintered compact 5b which consists of Li_2TiO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_3-yO_{12}$ ($M=$ aluminum or Ga, $0 \leq x \leq 0.4$, $0 < y \leq 0.6$). Li_2MnO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_3-yO_{12}$ ($M=$ aluminum or Ga, $0 \leq x \leq 0.4$, $0 < y \leq 0.6$) are arranged in a positive-electrode 3 side, and sintered compact 5b which consists of Li_2TiO_3 and $Li_{1+x+y}M_xTi_{2-x}Si_yP_3-yO_{12}$ ($M=$ aluminum or Ga, $0 \leq x \leq 0.4$, $0 < y \leq 0.6$) is arranged in a negative-electrode 6 side.

[0024] $Li_{1+x}Mn_{2-x}O_4$ ($0.05 \leq x \leq 0.2$) or $Li_{1+x}Ni_yMn_{2-x-y}O_4$ ($0 \leq x \leq 0.2$, $0.4 \leq y \leq 0.6$) which is the active material ingredient with which Li_2MnO_3 constitutes a positive electrode 3 here, It is used in order to join $Li_{1+x+y}M_xTi_{2-x}Si_yP_3-yO_{12}$ ($M=$ aluminum or Ga, $0 \leq x \leq 0.4$, $0 < y \leq 0.6$) which is the ingredient which constitutes solid electrolyte 5a.

[0025] Moreover, Li_2TiO_3 is used in order to join $Li_{1+x}Ti_{2-x}O_4$ ($0.25 \leq x \leq 0.40$) which is the active material ingredient which constitutes a negative electrode 6, and $Li_{1+x+y}M_xTi_{2-x}Si_yP_3-yO_{12}$ ($M=$ aluminum or Ga, $0 \leq x \leq 0.4$, $0 < y \leq 0.6$) which is the ingredient which constitutes solid electrolyte 5b.

[0026] The approach of sintering, after making the water or the organic solvent in which (1) shaping assistant was dissolved in order to produce a solid electrolyte 5 (5a, 5b) distribute solid electrolyte fine particles, adjusting a slurry, adding a direct or shaping assistant, corning the approach of judging and sintering after carrying out tape forming of this slurry and drying, or (2) solid-electrolyte fine particles, supplying to metal mold and carrying out pressing with a press machine etc. is used.

[0027] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.

[0028] The sintering conditions of a solid electrolyte 5, a positive electrode 3, and a negative electrode 6 are suitably chosen from 30 minutes within the limits of 30 hours according to the synthetic conditions of the presentation of an active material and a solid electrolyte, an active material, and a solid electrolyte, or the size of a sintered compact at 500 to 900 degrees C.

[0029] The positive-electrode current collection layer 2 and the negative-electrode current collection layer 7 are arranged for contact to the positive-electrode can 1, a positive electrode 3, or the negative-electrode can 8 and a negative electrode 6, and current collection, for example, consist conductive ingredients, such as gold, silver, copper, aluminum, nickel, and carbon, of vacuum evaporation or the thin film which carried out sputtering.

[0030] It is arranged in order that the positive-electrode can 1 and the negative-electrode can 8 may prevent inhibition of the charge-and-discharge reaction by the moisture in atmospheric air, and in order to use as each terminal of a positive electrode 3 and a negative electrode 6, for example, the sheet metal of metals, such as aluminum, copper, nickel, stainless steel, and titanium, is used.

[0031] In order that the insulating section 4 may prevent the short circuit of a positive electrode 3 and a negative electrode 6, it is arranged, for example, macromolecules, such as polyethylene, polypropylene, and polyimide, are used.

[0032] A sheathing package consists of a positive-electrode can 1, the insulating section 4, and a negative-electrode can 8.

[0033]

[Example 1] The laminating of the positive-electrode Plastic solid which consists of $Li_{1.1}Mn$

1.9O4, and the solid electrolyte Plastic solid by the side of the positive electrode which consists of Li2MnO3/Li1.31aluminum0.3Ti1.7Si01P2.99O12=10/90wt% is carried out. The laminating of the negative-electrode Plastic solid which consists of Li1.33Ti 1.67O4, and the solid electrolyte Plastic solid by the side of the negative electrode which consists of Li2TiO3/Li1.31aluminum0.3Ti1.7Si01P2.99O12=10/90wt% is carried out. Furthermore The solid electrolyte layer which consists of Li2MnO3/Li1.31aluminum0.3Ti1.7Si01P2.99O12=10/90wt%, and the solid electrolyte layer by the side of the negative electrode which consists of Li2TiO3/Li1.31aluminum0.3Ti1.7Si01P2.99O12=10/90wt% The solid electrolyte cell component was produced by carrying out a laminating so that it may ****, and processing at 850 degrees C for 10 hours.

[0034] As for the size of the produced solid electrolyte cell component, for the positive electrode, 250 micrometers and a solid electrolyte were [a total of 10 micrometers and the negative electrode of phi20mm and thickness] 250 micrometers.

[0035] After vapor-depositing gold to both sides of a solid electrolyte cell component and forming a phi18mm current collection layer in them, the solid electrolyte cell was produced by inserting in into a polyethylene ring with the outer diameter of 25mm, a bore [of 20.5mm], and a height of 550 micrometers, and inserting and carrying out thermocompression bonding to the aluminum sheet metal of two sheets in an argon.

[0036]

[The example 1 of a comparison] The solid electrolyte cell component was produced by carrying out the laminating of the positive-electrode Plastic solid which consists of Li1.1Mn 1.9O4, the solid electrolyte Plastic solid which consists of Li1.31aluminum0.3Ti1.7Si01P2.99O12, and the negative-electrode Plastic solid which consists of Li1.33Ti 1.67O4, and processing it at 850 degrees C for 10 hours.

[0037] The made solid electrolyte cell component had the weak solid electrolyte layer, therefore was that in which a positive electrode and a negative electrode tend to peel.

[0038] As for the size of the produced solid electrolyte cell component, for the positive electrode, 250 micrometers and a solid electrolyte were [a total of 10 micrometers and the negative electrode of phi20mm and thickness] 250 micrometers.

[0039] After vapor-depositing gold to both sides of a solid electrolyte cell component and forming a phi18mm current collection layer in them, dealing with it carefully, the solid electrolyte cell was produced by inserting in into a polyethylene ring with the outer diameter of 25mm, a bore [of 20.5mm], and a height of 550 micrometers, and inserting and carrying out thermocompression bonding to the aluminum sheet metal of two sheets in an argon.

[0040] Charge-and-discharge capacity was measured with the current density of 100microA/cm² about the produced solid electrolyte cell. The result is shown in Table 1.

[0041]

[Table 1]

実測容量 (正極基準)		実測容量 / 理論容量比 (正極基準)	
実施例1	10.5 mAh/g	95.5%	—
比較例1	動作しない	—	—

[0042] The positive-electrode sintered compact which consists of Li1.1Mn 1.9O4 as Table 1 shows, The solid electrolyte sintered compact which consists of Li1.31aluminum0.3Ti1.7Si01P2.99O12, As opposed to the example 1 of a comparison which consists of negative-electrode sintered compacts which consist of Li1.33Ti 1.67O4 not showing charge-and-discharge actuation While arranging the solid electrolyte which changes from Li2MnO3/Li1.31aluminum0.3Ti1.7Si01P2.99O12=10/90wt% to the positive-electrode side which consists of Li1.1Mn 1.9O4 The solid electrolyte cell of the example 1 which arranged the solid electrolyte which changes from Li2TiO3/Li1.31aluminum0.3Ti1.7Si01P2.99O12=10/90wt% to the negative-electrode side which consists of Li1.33Ti 1.67O4 shows charge-and-discharge actuation.

[0043] This is added to sintering of a solid electrolyte having the inadequate example 1 of a

comparison. Junction to the positive electrode which consists of $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ in an example 1 to a thing with the high interfacial resistance of an electrode and a solid electrolyte, and Li_2MnO_3 in a solid electrolyte, Junction to the negative electrode which consists of $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$, and Li_2TiO_3 in a solid electrolyte, Junction to Li_2MnO_3 in a positive-electrode side solid electrolyte, and $\text{Li}_{1.31}\text{aluminum}_{0.3}\text{Ti}_{1.7}\text{Si}_{0.1}\text{P}_{2.99}\text{O}_{12}$, And each of junction to Li_2TiO_3 in a negative-electrode side solid electrolyte and $\text{Li}_{1.31}\text{aluminum}_{0.3}\text{Ti}_{1.7}\text{Si}_{0.1}\text{P}_{2.99}\text{O}_{12}$ is good. The solid electrolyte sintered compact with high ionic conductivity with a sufficient therefore degree of sintering was not only obtained, but Li_2MnO_3 in a positive-electrode side solid electrolyte dissolves to $\text{Li}_{1.31}\text{aluminum}_{0.3}\text{Ti}_{1.7}\text{Si}_{0.1}\text{P}_{2.99}\text{O}_{12}$ in $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ in a positive electrode, and a solid electrolyte. When Li_2TiO_3 in a negative-electrode side solid electrolyte dissolves to $\text{Li}_{1.31}\text{aluminum}_{0.3}\text{Ti}_{1.7}\text{Si}_{0.1}\text{P}_{2.99}\text{O}_{12}$ in $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$ in a negative electrode, and a solid electrolyte, it is because the interfacial resistance of an electrode and a solid electrolyte is reduced.

[0044] In addition, the same effectiveness is checked even if it uses $\text{Li}_{1}\text{nickel}_{0.5}\text{Mn}_{1.5}\text{O}_4$ for positive active material.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view showing the example of a configuration of the solid electrolyte cell in this invention.

[Description of Notations]

1 [.. The insulating section (sheathing package), 5 / .. A solid electrolyte, 6 / .. A negative electrode, 7 / .. A negative-electrode current collection layer, 8 / .. Negative-electrode can (sheathing package)] A positive-electrode can (sheathing package), 2 .. A positive-electrode current collection layer, 3 .. A positive electrode, 4

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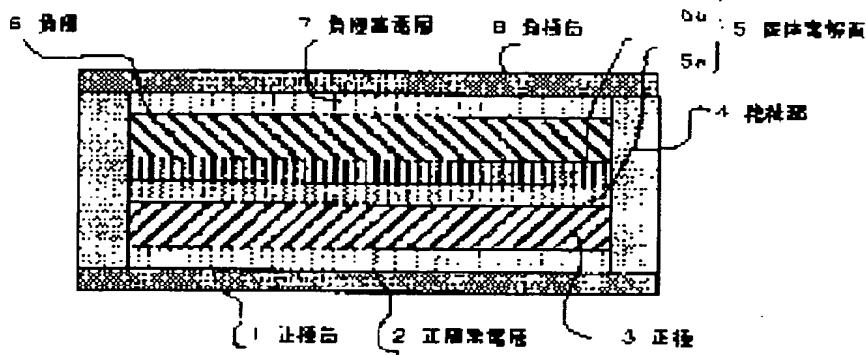
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DRAWINGS

[Drawing 1]



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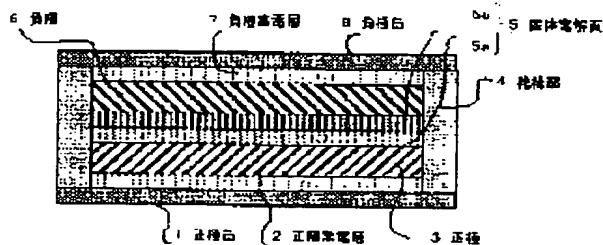
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(54)【発明の名称】 固体電解質電池

(57)【要約】

【課題】 従来、電極と固体電解質との接合が難しく、電極と固体電解質との界面抵抗が大きいという問題があった。

【解決手段】 スピネル系マンガン酸リチウムから成る正極とスピネル系チタン酸リチウムから成る負極とで固体電解質を挟持して外装パッケージ内に封入した固体電解質電池であって、上記固体電解質を $L_{1-x}MnO_3$ と $L_{1-x}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ ($M=A1$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体と、 $L_{1-x}TiO_3$ と $L_{1-x}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ ($M=A1$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体とで形成すると共に、上記正極側に前記 $L_{1-x}MnO_3$ と $L_{1-x}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ ($M=A1$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体を配設し、上記負極側に前記 $L_{1-x}TiO_3$ と $L_{1-x}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ ($M=A1$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体を配設した。



【特許請求の範囲】

【請求項1】スピネル系マンガン酸リチウムから成る正極とスピネル系チタン酸リチウムから成る負極とで固体電解質を挟持して外装パッケージ内に封入した固体電解質電池において、前記固体電解質を $L_{1-x}MnO_3$ と $L_{1-y}M_xTi_{2-y}Si_yP_{3-y}O_{12}$ ($M=Al$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体と、 $L_{1-x}TiO_3$ と $L_{1-y}M_xTi_{2-y}Si_yP_{3-y}O_{12}$ ($M=Al$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体とで形成すると共に、前記正極側に前記 $L_{1-x}MnO_3$ と $L_{1-y}M_xTi_{2-y}Si_yP_{3-y}O_{12}$ ($M=Al$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体を配設し、前記負極側に前記 $L_{1-x}TiO_3$ と $L_{1-y}M_xTi_{2-y}Si_yP_{3-y}O_{12}$ ($M=Al$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体を配設したことを特徴とする固体電解質電池。

【請求項2】前記正極を $L_{1-x}Mn_{2-x}O_4$ ($0.05 \leq x \leq 0.2$) または $L_{1-x}Ni_xMn_{2-x}O_4$ ($0 \leq x \leq 0.2$ 、 $0.4 \leq y < 0.6$) 焼結体で形成すると共に、前記負極を $L_{1-x}Ti_{2-x}O_4$ ($0.25 \leq x \leq 0.40$) 焼結体で形成したことを特徴とする固体電解質電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は固体電解質電池に関し、特に正極と負極とで固体電解質を挟持して外装パッケージ内に封入した固体電解質電池に関する。

【0002】

【従来の技術および発明が解決しようとする課題】近年のノートパソコンや携帯電話等の携帯用電子機器の高性能化と小型化にはめざましいものがある。これら携帯機器に使用される電池では、より一層の高エネルギー密度化と小型化が要求されている。

【0003】このような要求に応えるものとして、リチウムイオンの脱挿入を利用したリチウム二次電池が盛んに研究されている。

【0004】しかしながら、従来のリチウム二次電池は非水電解液を使用しているため、電解液の漏液や発火といった製品安全上無視できない問題がある。

【0005】このような問題を解決するために、電解液を一切使わない固体電解質電池の開発が検討されている。

【0006】固体電解質としては、例えば特開平10-97811号公報に記載された $L_{1-x}M_xTi_{2-y}Si_yP_{3-y}O_{12}$ ($M=Al$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) で表される組成を持ったリチウムイオン伝導性ガラスセラミックスが提唱されている。このガラスセラミックスは、構成原料を溶融した後、熱処理によって結晶析出させるため、粒界が少なく、したがって

粒界抵抗が低く、その結果 $1 \times 10^{-3} S/cm$ という高いリチウムイオン伝導度が得られるという利点がある。

【0007】しかしながら、特開平10-97811号公報では、溶融のための熱処理が $1450^{\circ}C$ で行われ、結晶析出のための熱処理が $800^{\circ}C$ と $1000^{\circ}C$ の2段階で行われることから、非常に高温での処理を必要とする。これに対し、リチウム二次電池で使用される電極活性物質は、 $700^{\circ}C$ からせいぜい $900^{\circ}C$ の温度で熱処理されるものが多い。したがって、電極と固体電解質とを接合するさいの熱処理温度を電極活性物質に合わせざるを得ないため、電極とガラスセラミックスから成る固体電解質との接合が難しく、今のところ両者を良好に接合できた固体電解質電池は得られていない。

【0008】また、特開平5-299101号公報においては、 $L_{1-(x+y)}M_xTi_{2-y}(PO_4)_3$ (M は1価または2価の陽イオン、 M が1価の陽イオンのとき $n=1$ 、 M が2価の陽イオンのとき $n=2$ 、 x は $0.1 \sim 0.5$) を焼結した固体電解質も提唱されているが、この焼結温度も $1000^{\circ}C$ から $1200^{\circ}C$ と高いため、電極との接合は困難である。

【0009】一方、電極と固体電解質を密着させて、界面抵抗の低い固体電解質電池を提供するための方法が提案されている。

【0010】例えば特開平6-111831号公報では、 MnO_2 またはアルカリ金属マンガン複合酸化物から成る正極の表面に、リチウム化合物を反応させて固体電解質の $L_{1-x}MnO_3$ を生成させることを提唱している。この方法によれば、正極と固体電解質の密着性が良く、接触面積が大きいため、界面抵抗が低いという利点がある。

【0011】しかしながら、特開平6-111831号公報では、固体電解質のイオン伝導度が低いため、活性物質が本来持つ容量を十分に引き出せていない上に、負極に金属リチウムを使用しているため、負極と固体電解質との接觸は金属リチウムの延展性に依存しており、正極側に比べると界面抵抗は高くならざるを得ないという問題がある。

【0012】本発明はこのような従来技術の問題点に鑑みてなされたものであり、電極と固体電解質との接合が難しく、また電極と固体電解質との界面抵抗が大きいという従来の問題点を解消した固体電解質電池を提供することを目的とする。

【0013】

【課題を解決するための手段】上記目的を達成するため、本発明に係る固体電解質電池では、スピネル系マンガン酸リチウムから成る正極とスピネル系チタン酸リチウムから成る負極とで固体電解質を挟持して外装パッケージ内に封入した固体電解質電池において、前記固体電解質を $L_{1-x}MnO_3$ と $L_{1-y}M_xTi_{2-y}Si_yP_{3-y}O_{12}$ ($M=Al$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体と、 $L_{1-x}TiO_3$ と $L_{1-y}M_xTi_{2-y}Si_yP_{3-y}O_{12}$ ($M=Al$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体とで形成すると共に、前記正極側に前記 $L_{1-x}MnO_3$ と $L_{1-y}M_xTi_{2-y}Si_yP_{3-y}O_{12}$ ($M=Al$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体を配設し、前記負極側に前記 $L_{1-x}TiO_3$ と $L_{1-y}M_xTi_{2-y}Si_yP_{3-y}O_{12}$ ($M=Al$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体を配設したことを特徴とする。

0. 6) とから成る焼結体と、 Li_2TiO_3 と $\text{Li}_{1-x}\text{M}_x\text{Ti}_{2-y}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{Al}$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体とで形成すると共に、前記正極側に前記 Li_2MnO_3 と $\text{Li}_{1-x}\text{M}_x\text{Ti}_{2-y}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{Al}$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体を配設し、前記負極側に前記 Li_2TiO_3 と $\text{Li}_{1-x}\text{M}_x\text{Ti}_{2-y}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{Al}$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体を配設したことを特徴とする。

【0014】上記固体電解質電池では、前記正極を $\text{Li}_{1-x}\text{Mn}_{2-y}\text{O}_4$ ($0.05 \leq x \leq 0.2$) または $\text{Li}_{1-x}\text{Ni}_x\text{Mn}_{2-y}\text{O}_4$ ($0 \leq x \leq 0.2$ 、 $0.4 \leq y < 0.6$) 焼結体で形成すると共に、前記負極を $\text{Li}_{1-x}\text{Ti}_{2-y}\text{O}_4$ ($0.25 \leq x \leq 0.40$) 焼結体で形成することが望ましい。

【0015】

【発明の実施の形態】以下、本発明の実施形態を説明する。図1は本発明の固体電解質電池の構成例を示す断面図であり、1は正極缶、2は正極集電層、3は正極、4は絶縁部、5は固体電解質、6は負極、7は負極集電層、8は負極缶である。正極缶1と負極缶8と絶縁部4とで外装パッケージが構成される。

【0016】正極3はスピネル系マンガン酸リチウムの焼結体から成る。このようなスピネル系マンガン酸リチウムには $\text{Li}_{1-x}\text{Mn}_{2-y}\text{O}_4$ ($0.05 \leq x \leq 0.2$) または $\text{Li}_{1-x}\text{Ni}_x\text{Mn}_{2-y}\text{O}_4$ ($0 \leq x \leq 0.2$ 、 $0.4 \leq y < 0.6$) がある。

【0017】ここで、 $\text{Li}_{1-x}\text{Mn}_{2-y}\text{O}_4$ ($0.05 \leq x \leq 0.2$) の x が 0.05 より小さいと充放電時の膨脹収縮を抑える効果が十分でなく、また、 x が 0.2 より大きいと充放電容量の低下が顕著であるため、正極3に用いる利点が損なわれる。

【0018】また、 $\text{Li}_{1-x}\text{Ni}_x\text{Mn}_{2-y}\text{O}_4$ ($0 \leq x \leq 0.2$ 、 $0.4 \leq y < 0.6$) はより高電位の正極材料であるが、この y が 0.4 より小さいと、 $\text{Li}_{1-x}\text{Mn}_{2-y}\text{O}_4$ ($0.05 \leq x \leq 0.2$) に比較して十分な高電位が得られず、また、 y が 0.6 以上になると Ni が固溶しきらず、不純物相を生成するので好ましくない。

【0019】負極6はスピネル系チタン酸リチウムの焼結体から成る。このようなスピネル系チタン酸リチウムには $\text{Li}_{1-x}\text{Ti}_{2-y}\text{O}_4$ ($0.25 \leq x \leq 0.40$) がある。

【0020】ここで、 $\text{Li}_{1-x}\text{Ti}_{2-y}\text{O}_4$ ($0.25 \leq x \leq 0.40$) の x が 0.25 より小さいと、充放電時の膨脹収縮を抑える効果が十分でなく、また、 x が 0.4 より大きいとリチウムが固溶しきらず、不純物相を生成するので好ましくない。

【0021】正極3および負極6を作製するには、

(1) 成形助剤を溶解させた水または有機溶剤に活物質

粉体を分散させてスラリーを調整し、このスラリーをテープ成形して乾燥した後に裁断して焼結する方法、あるいは(2) 活物質粉体を直接あるいは成形助剤を加えて造粒して金型に投入してプレス機で加圧成形した後に焼結する方法などが用いられる。

【0022】ここで使用可能な成形助剤としては、例えばポリアクリル酸、カルボキシメチルセルロース、ポリビニルアルコール、ジアセチルセルロース、ヒドロキシプロピルセルロース、ポリブチラールなどの1種もしくは2種以上の混合物が挙げられる。

【0023】固体電解質5は、 $\text{Li}_{1-x}\text{MnO}_3$ および $\text{Li}_{1-x}\text{M}_x\text{Ti}_{2-y}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{Al}$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) から成る焼結体5aと、 $\text{Li}_{1-x}\text{TiO}_3$ および $\text{Li}_{1-x}\text{M}_x\text{Ti}_{2-y}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{Al}$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) から成る焼結体5bとから成る。 $\text{Li}_{1-x}\text{MnO}_3$ および $\text{Li}_{1-x}\text{M}_x\text{Ti}_{2-y}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{Al}$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) から成る焼結体5aが正極3側に配設され、 $\text{Li}_{1-x}\text{TiO}_3$ および $\text{Li}_{1-x}\text{M}_x\text{Ti}_{2-y}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{Al}$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) から成る焼結体5bが負極6側に配設される。

【0024】ここで、 $\text{Li}_{1-x}\text{MnO}_3$ は、正極3を構成する活物質材料である $\text{Li}_{1-x}\text{Mn}_{2-y}\text{O}_4$ ($0.05 \leq x \leq 0.2$) または $\text{Li}_{1-x}\text{Ni}_x\text{Mn}_{2-y}\text{O}_4$ ($0 \leq x \leq 0.2$ 、 $0.4 \leq y < 0.6$) と、固体電解質5aを構成する材料である $\text{Li}_{1-x}\text{M}_x\text{Ti}_{2-y}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{Al}$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とを接合するために用いられる。

【0025】また、 $\text{Li}_{1-x}\text{TiO}_3$ は、負極6を構成する活物質材料である $\text{Li}_{1-x}\text{Ti}_{2-y}\text{O}_4$ ($0.25 \leq x \leq 0.40$) と、固体電解質5bを構成する材料である $\text{Li}_{1-x}\text{M}_x\text{Ti}_{2-y}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($\text{M}=\text{Al}$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とを接合するために用いられる。

【0026】固体電解質5(5a、5b)を作製するには、(1) 成形助剤を溶解させた水または有機溶剤に固体電解質粉体を分散させてスラリーを調整し、このスラリーをテープ成形して乾燥した後に裁断して焼結する方法、あるいは、(2) 固体電解質粉体を直接あるいは成形助剤を加えて造粒して金型に投入してプレス機で加圧成形した後に焼結する方法などが用いられる。

【0027】ここで使用可能な成形助剤としては、例えばポリアクリル酸、カルボキシメチルセルロース、ポリビニルアルコール、ジアセチルセルロース、ヒドロキシプロピルセルロース、ポリブチラールなどの1種もしくは2種以上の混合物が挙げられる。

【0028】固体電解質5、正極3、および負極6の焼結条件は、 500°C から 900°C で 30 分から 30 時間の範囲内で、活物質および固体電解質の組成、活物質お

より固体電解質の合成条件、あるいは焼結体のサイズに応じて適宜選択される。

【0029】正極集電層2および負極集電層7は、正極缶1と正極3、あるいは負極缶8と負極6との接触と集電のために配置され、例えば金、銀、銅、アルミニウム、ニッケル、カーボンなどの導電性材料を蒸着あるいはスパッタリングした薄膜から成る。

【0030】正極缶1および負極缶8は、大気中の水分による充放電反応の阻害を防ぐため、および正極3と負極6のそれぞれの端子として用いるために配置され、例えばアルミニウム、銅、ニッケル、ステンレススチール、チタンなどの金属の薄板が用いられる。

【0031】絶縁部4は、正極3と負極6との短絡を防ぐために配置され、例えばポリエチレン、ポリプロピレン、ポリイミドなどの高分子が用いられる。

【0032】正極缶1、絶縁部4、負極缶8とで外装パッケージが構成される。

【0033】

【実施例1】 $\text{Li}_{1.1} \text{Mn}_{1.9} \text{O}_4$ から成る正極成形体と $\text{Li}_2 \text{MnO}_3 / \text{Li}_{1.31} \text{Al}_{0.3} \text{Ti}_{1.7} \text{Si}_{0.1} \text{P}_{2.99} \text{O}_{12} = 10 / 90 \text{wt\%}$ から成る正極側の固体電解質成形体とを積層し、 $\text{Li}_{1.33} \text{Ti}_{1.67} \text{O}_4$ から成る負極成形体と $\text{Li}_2 \text{TiO}_3 / \text{Li}_{1.31} \text{Al}_{0.3} \text{Ti}_{1.7} \text{Si}_{0.1} \text{P}_{2.99} \text{O}_{12} = 10 / 90 \text{wt\%}$ から成る負極側の固体電解質成形体とを積層して、さらに $\text{Li}_2 \text{MnO}_3 / \text{Li}_{1.31} \text{Al}_{0.3} \text{Ti}_{1.7} \text{Si}_{0.1} \text{P}_{2.99} \text{O}_{12} = 10 / 90 \text{wt\%}$ から成る固体電解質層と $\text{Li}_2 \text{TiO}_3 / \text{Li}_{1.31} \text{Al}_{0.3} \text{Ti}_{1.7} \text{Si}_{0.1} \text{P}_{2.99} \text{O}_{12} = 10 / 90 \text{wt\%}$ から成る負極側の固体電解質層とが接するように積層して、850°Cで10時間処理することにより、固体電解質電池素子を作製した。

【0034】作製した固体電解質電池素子のサイズは ϕ *

実測容量(正極基準)	実測容量/理論容量比(正極基準)
実施例1: 105mAh/g	95.5%
比較例1: 動作しない	—

【0042】表1からわかる通り、 $\text{Li}_{1.1} \text{Mn}_{1.9} \text{O}_4$ から成る正極焼結体と、 $\text{Li}_{1.31} \text{Al}_{0.3} \text{Ti}_{1.7} \text{Si}_{0.1} \text{P}_{2.99} \text{O}_{12}$ から成る固体電解質焼結体と、 $\text{Li}_{1.33} \text{Ti}_{1.67} \text{O}_4$ から成る負極焼結体とで構成される比較例1が充放電動作を示さないのに対し、 $\text{Li}_{1.1} \text{Mn}_{1.9} \text{O}_4$ から成る正極側に $\text{Li}_2 \text{MnO}_3 / \text{Li}_{1.31} \text{Al}_{0.3} \text{Ti}_{1.7} \text{Si}_{0.1} \text{P}_{2.99} \text{O}_{12} = 10 / 90 \text{wt\%}$ から成る固体電解質を配設すると共に、 $\text{Li}_{1.33} \text{Ti}_{1.67} \text{O}_4$ から成る負極側に $\text{Li}_2 \text{TiO}_3 / \text{Li}_{1.31} \text{Al}_{0.3} \text{Ti}_{1.7} \text{Si}_{0.1} \text{P}_{2.99} \text{O}_{12} = 10 / 90 \text{wt\%}$ から成る固体電解質を配設した実施例1の固体電解質電池では充放電動作を示している。

【0043】これは、比較例1が固体電解質の焼結が不十分であることに加えて、電極と固体電解質との界面抵

(4) 6

* 20mm、厚さは正極が250μm、固体電解質が計10μm、負極が250μmであった。

【0035】固体電解質電池素子の両面に金を蒸着して、 $\phi 18 \text{mm}$ の集電層を形成した後、アルゴン中にて、外径25mm、内径20.5mm、高さ550μmのポリエチレンリング中にはめ込み、二枚のアルミニウム薄板に挟んで熱圧着することで固体電解質電池を作製した。

【0036】

10 【比較例1】 $\text{Li}_{1.1} \text{Mn}_{1.9} \text{O}_4$ から成る正極成形体と、 $\text{Li}_{1.31} \text{Al}_{0.3} \text{Ti}_{1.7} \text{Si}_{0.1} \text{P}_{2.99} \text{O}_{12}$ から成る固体電解質成形体と、 $\text{Li}_{1.33} \text{Ti}_{1.67} \text{O}_4$ から成る負極成形体とを積層して、850°Cで10時間処理することにより、固体電解質電池素子を作製した。

【0037】できた固体電解質電池素子は固体電解質層が脆く、そのため、正極と負極とがはがれやすいものであった。

【0038】作製した固体電解質電池素子のサイズは $\phi 20 \text{mm}$ 、厚さは正極が250μm、固体電解質が計10μm、負極が250μmであった。

【0039】注意深く取り扱いながら、固体電解質電池素子の両面に金を蒸着して、 $\phi 18 \text{mm}$ の集電層を形成した後、アルゴン中にて、外径25mm、内径20.5mm、高さ550μmのポリエチレンリング中にはめ込み、二枚のアルミニウム薄板に挟んで熱圧着することで固体電解質電池を作製した。

【0040】作製した固体電解質電池について100μA/cm²の電流密度で充放電容量を測定した。その結果を表1に示す。

【0041】

【表1】

抗が高いのに対し、実施例1においては $\text{Li}_{1.1} \text{Mn}_{1.9} \text{O}_4$ から成る正極と固体電解質中の $\text{Li}_2 \text{MnO}_3$ との接合、 $\text{Li}_{1.33} \text{Ti}_{1.67} \text{O}_4$ から成る負極と固体電解質中の $\text{Li}_2 \text{TiO}_3$ との接合、正極側固体電解質中の $\text{Li}_2 \text{MnO}_3$ と $\text{Li}_{1.31} \text{Al}_{0.3} \text{Ti}_{1.7} \text{Si}_{0.1} \text{P}_{2.99} \text{O}_{12}$ との接合、および負極側固体電解質中の $\text{Li}_2 \text{TiO}_3$ と $\text{Li}_{1.31} \text{Al}_{0.3} \text{Ti}_{1.7} \text{Si}_{0.1} \text{P}_{2.99} \text{O}_{12}$ との接合がいずれも良好であり、焼結性が良く、したがってイオン伝導度の高い固体電解質焼結体が得られただけでなく、正極側固体電解質中の $\text{Li}_2 \text{MnO}_3$ が正極中の $\text{Li}_{1.1} \text{Mn}_{1.9} \text{O}_4$ および固体電解質中の $\text{Li}_{1.31} \text{Al}_{0.3} \text{Ti}_{1.7} \text{Si}_{0.1} \text{P}_{2.99} \text{O}_{12}$ へ固溶し、負極側固体電解質中の $\text{Li}_2 \text{TiO}_3$ が負極中の $\text{Li}_{1.33} \text{Ti}_{1.67} \text{O}_4$ および固体電解質中の $\text{Li}_{1.31} \text{Al}_{0.3} \text{Ti}_{1.7} \text{Si}_{0.1} \text{P}_{2.99} \text{O}_{12}$ へ固溶

することにより、電極と固体電解質との界面抵抗が低減されていることによる。

【0044】なお、正極活物質に $Li_{1.31}Ni_{0.5}Mn_{1.5}O_4$ を用いても同様の効果が確認される。

【0045】

【発明の効果】以上のように、本発明に係る固体電解質電池によれば、固体電解質を $Li_{1.2}MnO_3$ と $Li_{1-x-y}M_xTi_{2-y}Si_yP_{3-y}O_{12}$ ($M = Al$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体と、 $Li_{1.2}TiO_3$ と $Li_{1-x-y}M_xTi_{2-y}Si_yP_{3-y}O_{12}$ ($M = Al$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体とで形成すると共に、正極側に上記 $Li_{1.2}MnO_3$ と $Li_{1-x-y}M_xTi_{2-y}Si_yP_{3-y}O_{12}$ ($M = Al$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体を配設し、負極側に上記 $Li_{1.2}TiO_3$ と $Li_{1-x-y}M_xTi_{2-y}Si_yP_{3-y}O_{12}$ ($M = Al$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) とから成る焼結体を配設したことから、 $Li_{1.1}Mn_{1.5}O_4$ から成る正極と固体電解質中の $Li_{1.2}MnO_3$ との接合、 $Li_{1.33}Ti_{1.67}O_4$ から成る負極と固体電解質中の $Li_{1.2}TiO_3$ と $Li_{1-x-y}M_xTi_{2-y}Si_yP_{3-y}O_{12}$ ($M = Al$ または Ga 、 $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$) との接合、正極側固体電解質中の $Li_{1.2}MnO_3$ と *

* $Li_{1.31}Al_{0.3}Ti_{1.7}Si_{0.1}P_{2.99}O_{12}$ との接合、負極側固体電解質中の $Li_{1.2}TiO_3$ と $Li_{1.31}Al_{0.3}Ti_{1.7}Si_{0.1}P_{2.99}O_{12}$ との接合がいずれも良好であることにより、十分に高い電流密度の下でも正常に動作する電池を供することができる。

【0046】また、正極をスピネル系マンガン酸リチウムで形成すると共に、負極をスピネル系チタン酸リチウムで形成したことから、これら活物質の充放電時の膨脹収縮が全くないかあるいはほとんど問題にならない程度に小さいため、電極と固体電解質との界面の接触が損なわれることがなく、したがって安定した充放電挙動を示す固体電化質電池を提供することができる。

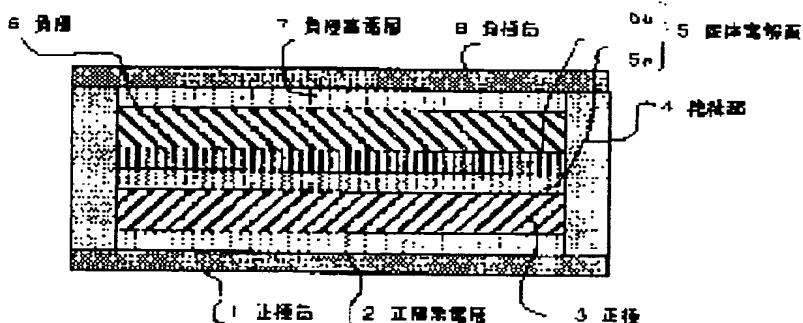
【図面の簡単な説明】

【図1】本発明における固体電解質電池の構成例を示す断面図である。

【符号の説明】

1……正極缶（外装パッケージ）、2……正極集電層、3……正極、4……絶縁部（外装パッケージ）、5……固体電解質、6……負極、7……負極集電層、8……負極缶（外装パッケージ）

【図1】



フロントページの続き

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